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Oxide-ceramic electrolyte layers for all-solid-state lithium batteries

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Introduction

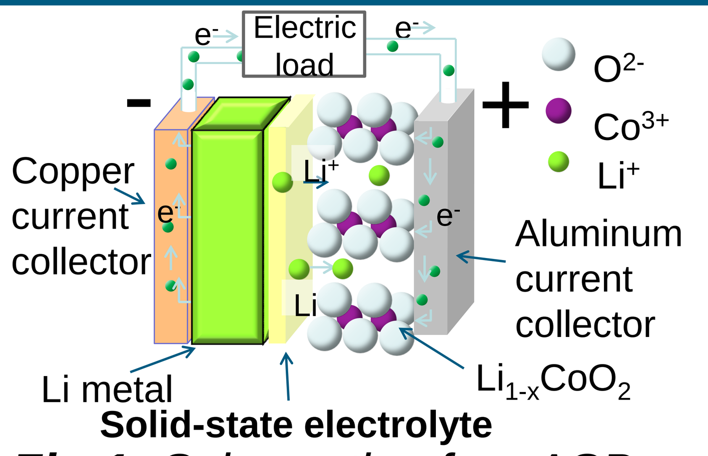

Fig.1: *Schematic of an ASB.*

Electricity generated from renewable energy sources gained much importance in our society. Thus requirements for electrical grid storage and the related safety aspects have risen. Major safety issues of conventional Li-ion batteries are associated with the use of organic liquid electrolytes. As an alternative, all-solid-state batteries (ASB), having one of the most promising oxide materials, $Li_7La_3Zr_2O_{12}$ (LLZ), are investigated. LLZ is an ionic conductor with a good thermal and electrochemical stability and chemical compatibility with metallic lithium. The ion conductivity can be further improved by partial substitution of Al, Ta or Y.

Motivation

- **Proof of concept exists:** prototype all-solid-state cell from bulk Ta-LLZ (LCO|Ta-LLZ|Li) that was able to light up an LED at 22°C.
- **Current tasks:**
  - solid electrolyte materials need to be optimized by Al-, Ta- and Y- substitution in lattice sites
  - bridging between lab scale and industrial application by large size LLZ functional layers, fabricated using established technologies.

Methods

Material preparation:

- **Solid-state reaction**
  - Stoichiometric composition out of oxide starting materials
  - Heat treatment to form highly conductive cubic -LLZ phase
  - Structure stabilization and conductivity increased by Al-, Ta- and Y-substitution

- **Spray pyrolysis technique**
  - 1.6 kg of Al-LLZ were synthesized from solution of starting materials at once
  - subsequently ball milling and heat treatment to form highly conductive cubic -LLZ phase.

Solid-electrolyte processing:

- **Tape casting**
  - Established, reproducible and up-scalable technology.
  - Slurry development and subsequent sintering studies of tape casted LLZ-films.

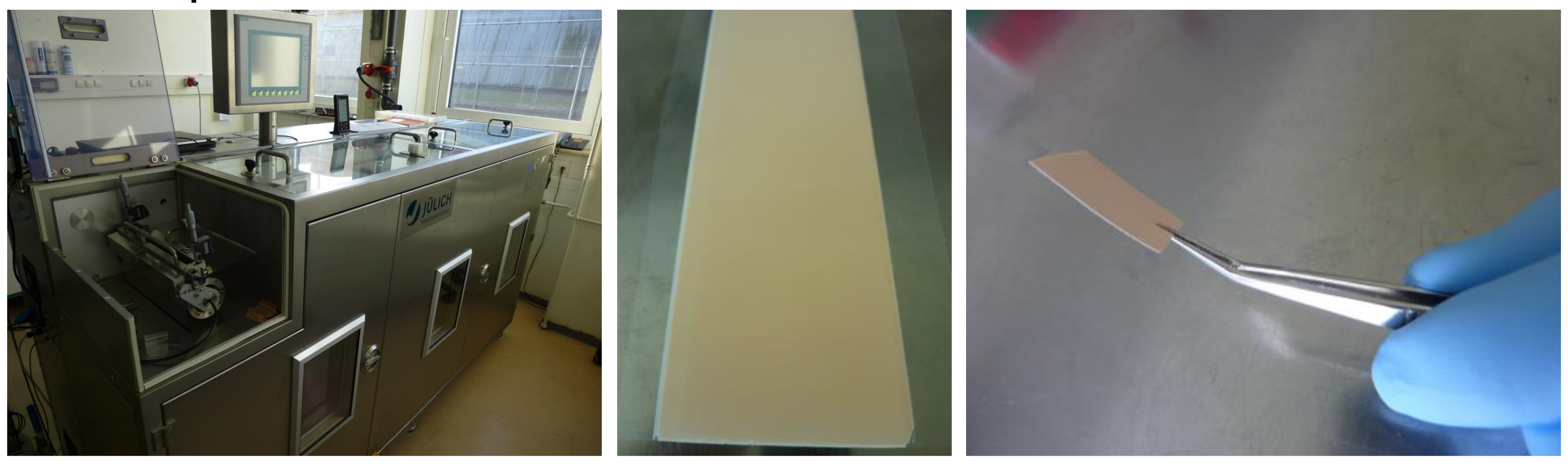

Fig.2: *A tape casting line at IEK-1 **(l.)** can be used for large scale tape casting. Al-LLZ tapes were successfully processed by tape casting with a gap size of 250 µm **(m.)** and 500 µm. Solid electrolytes with a green tape thickness of 90 µm **(r.)** and 180 µm were used for further sintering studies.*

Results

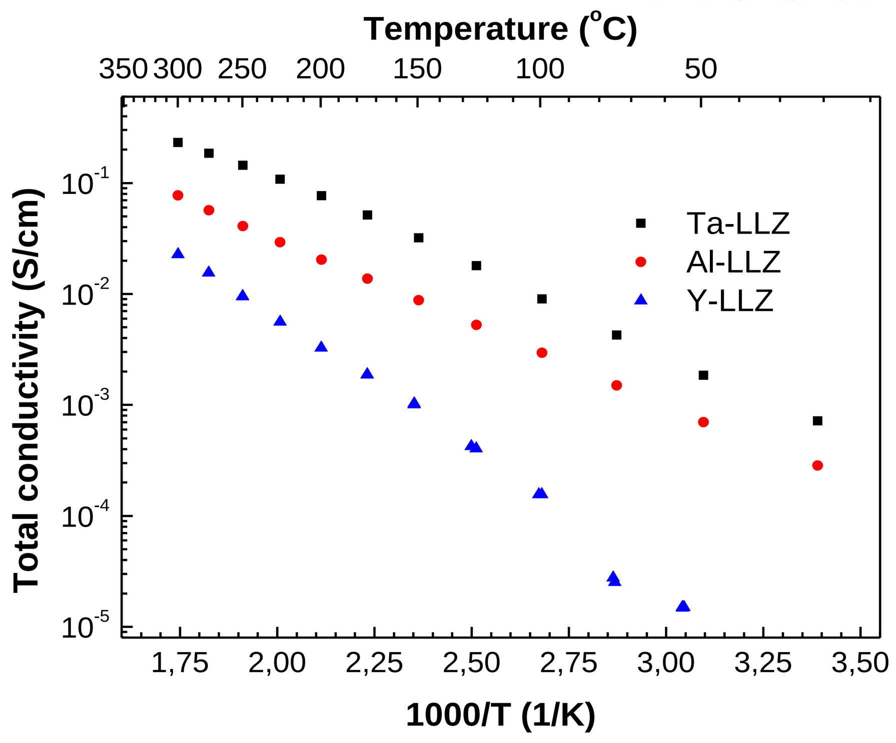

Fig.3: *Temperature dependence of the total ionic conductivity of Al-, Ta- and Y-substituted LLZ. Ta-substituted LLZ shows the highest total ionic conductivity among the three materials. The total conductivity was derived from impedance spectroscopy (1MHz-1Hz, amplitude: 20 mV/mm, temperature range: 22-300°C).*

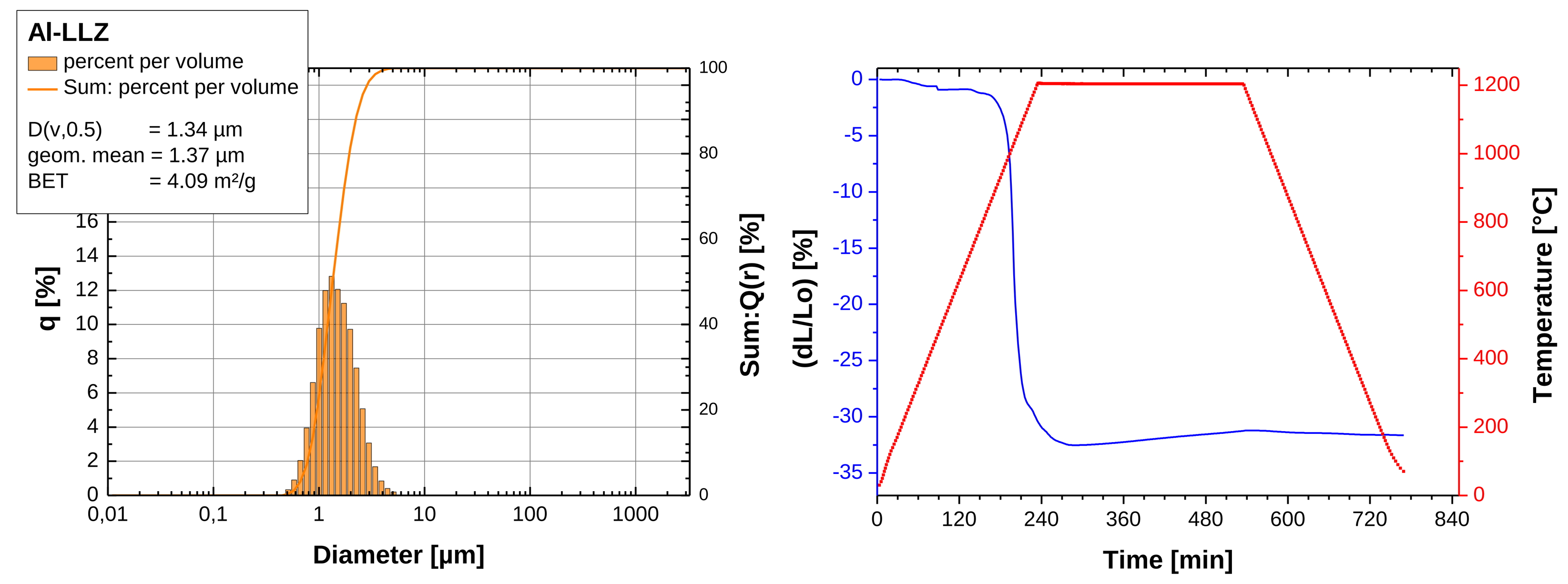

Fig.4: *1.6 kg of Al-LLZ were synthesized by spray pyrolysis and subsequently ball milled. The obtained powder has a mono-modal particle size distribution **(l.)** and shrinks approx. 30 Vol-% during sintering at 1000°C **(r.)**.*

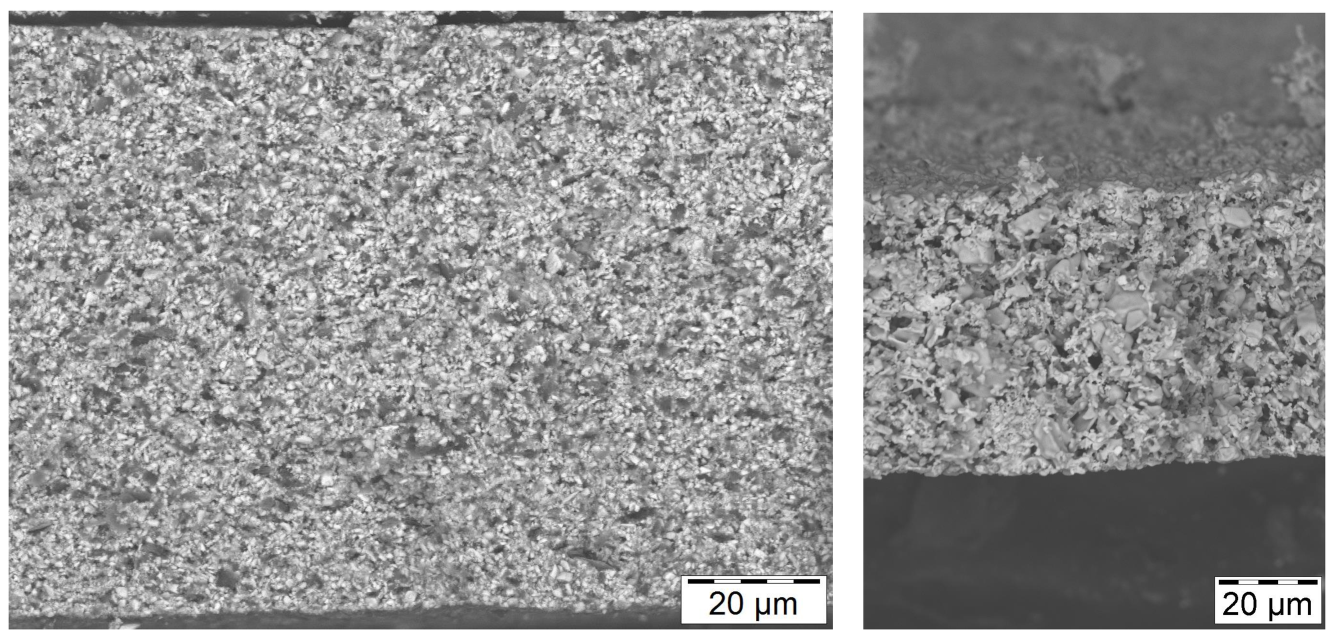

Fig.5: *By evaluation of SEM images of Al-LLZ green tape (90 µm thick, 48 % organic content) **(l.)** and sintered Al-LLZ samples (57 µm thickness after sintering, 13.9 % porosity) **(r.)** , the densification of the solid electrolyte film and its particle growth can be observed (2000x magnification; $V_{acceleration}$ = 15 kV).*

Conclusion

- Al-, Ta- and Y-substituted LLZ were synthesized and investigated. Ta-LLZ shows the highest total conductivity ($\sigma_{ion,RT} \approx 10^{-3}$ S/cm).
- As a first step 1.6 kg Al-LLZ was synthesized at once and can be processed by tape casting to obtain solid electrolyte tapes of 57 µm thickness and 13.9% porosity.

→Further sintering studies needed to increase density and reduce phase impurities of sintered AL-LLZ tapes.

→Ta-LLZ will be synthesized via spray pyrolysis to obtain highly conductive solid electrolyte in the scale of kilograms for best performing oxide-ceramic solid electrolyte layer in ASB application.

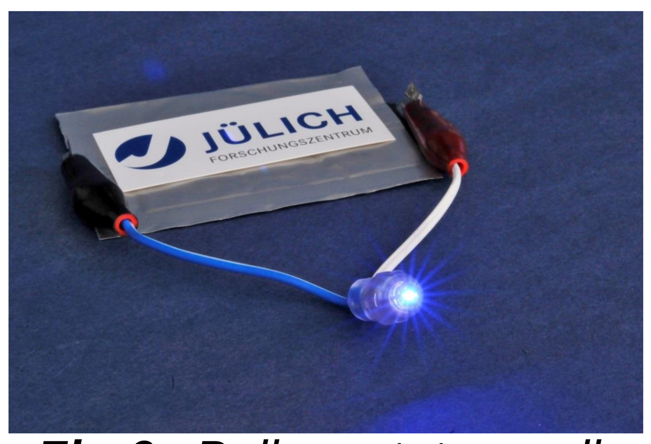

Fig.6: *Bulk prototype all-solid-state lithium battery.*

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